ELECTROCHEMICAL DEGRADATION OF REACTIVE BLUE 19 DYE IN TEXTILE WASTEWATER

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ABSTRACT

Textile wastewater is notoriously known to contain strong colour, a highly fluctuating pH and significant COD (Chemical Oxygen Demand) values. Because of these characteristics, treatment of these effluents has been rather difficult. Traditional methods for dealing with textile wastewater consist of various combinations of biological, physical and chemical methods. Because of the large variability of the composition of textile wastewaters, most of these traditional methods are becoming inadequate. The aim of this work was to use an electrochemical procedure to treat used dyebaths and cyclic voltammetry (CV) technique for dye degradation study. Electrolysis can be an adequate process for colour removal as well organics pollutants and CV is an important tool for redox reactions interpretation. Electrochemical treatment results show significant decrease on COD values, for the different values of dye concentration and several applied potentials. Progressive colour removal and dye degradation can be achieved for different values of dye concentration. Depending on electrolysis time and applied potential, total decolouration can be attained.

KEYWORDS
Electrochemical oxidation, colour removal, anthraquinone dye, cyclic voltammetry, Reactive Blue 19

1. INTRODUCTION

Textile industries consume large volumes of water and chemicals in wet processing of textiles. The chemical products used are very diverse in composition, from inorganic compounds to polymers and other organic products [1]. In general, the final textile waste effluent can be broadly categorized into three types of wastewater according to their COD content. Some characteristics of typical textile wastewater are presented in Table 1 [2].

Table 1 – Some characteristics of typical textile effluents

Type	COD (mgL^{-1})	Conductivity (μScm^{-1})
High strengh	1500	2900
Medium strengh	970	2500
Low strengh	460	2100

The presence of dyes in textile effluents is also common and highly visible. Depending on the type of dyestuff used, the colour of the wastewater can change from day to day, or even several times a day because the dyestuff used in the dyeing process changes frequently due to customer's requirements. The large pH swing in the textile wastewater (can change from 2 to over 12) is another strong negative point. This variation is primarily caused by different kinds of dyestuff used in the dyeing process.

As most dyes usually occur at low concentrations, it may be presumed that removing it from wastewater is not particularly difficult [3]. However, due to their chemical structure, such as acidic, basic, disperse, azo, diazo, anthraquinone based, dyes are resistant to fading on exposure to light, water or chemical compounds action. Anthraquinone based dyes are most resistant to degradation due to the fused aromatic ring structure.

Different methods are commonly used to remove colour from textile wastewater: chemical, physical and biological. Biological methods are generally cheap and simple to apply and have been applied to remove organics and colour of textile wastewater. But the refractory pollutants caused by textiles industries cannot easily be degraded by traditional biological process and remain in the effluent. Conventional aerobic biological process cannot readily treat textile wastewater because most commercial dyes are toxic to the organisms used. So, a physical/chemical method must be used. Current physical/chemical methods of dye removal from textile effluents are presented in Table 2 [1].

Table 2 – Some of the current physical/chemical methods of dye removal from textile effluents

Physical/chemical methods	Advantages	Disadvantages
Fenton's reagent	Effective colour removal	Sludge production
Photochemical	No sludge production	Formation of by-products
Electrochemical treatment	Non-hazardous breakdown compounds	Cost of electricity
Activated carbon	Good removal of wide variety of dyes	Very expensive
Peat	Good adsorbent due to cellular structure	Specific surface areas for adsorption are lower than activated carbon
Wood chips	Good sorption capacity for acid dyes	Requires long retention times
Silica gel	Effective for basic dye removal	Side reactions
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration of adsorbent	Not effective for all dyes
Ozonation	Applied in gaseous state: no alteration of volume	Short half-life (20 min)
Electrokinetic coagulation	Economically feasible	High sludge production

Electrochemical oxidation is a relatively new technique, developed in the 90's. It's an effective method for colour removal; there is little or no consumption of chemicals, no sludge production and degradation of recalcitrant pollutants can be achieved, including polyaromatic organic compounds, like anthraquinone-based compounds [4]. It is considered as one of the advanced oxidation processes, potentially a powerful method of pollution control, offering high removal efficiencies [5].

The aim of this work was to use an electrochemical procedure to treat used dyebaths containing NaCl as electrolyte, with no further addition of chemicals, and to use cyclic voltammetry (CV) technique for dye degradation study. Electrolysis can be an adequate process for colour removal as well organic pollutants and CV is an important tool for redox reactions interpretation.

Reactive Blue 19 dye, presented in Figure 1, is an anthraquinone-based vinylsulphone dye, very important in dyeing of cellulosic fibres.

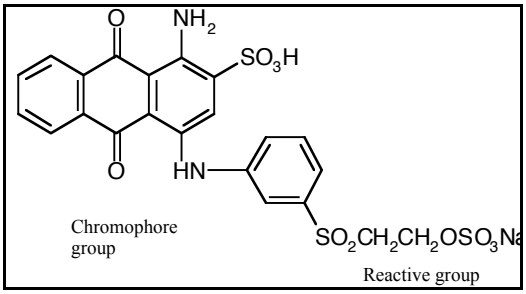

Figure 1 – Molecular structure of C.I. Reactive Blue 19

The extremely attractive bright blue hue combined with excellent light fastness could not be challenged by other reactive blue dyes for many years [6]. Fixation of the dye molecule onto the fibre occurs via covalent bonding by a nucleophilic addition mechanism at the hydroxyl group on cellulose. Stable bonds are formed.

However, during the alkaline dyeing process, hydrolysis of the dye occurs as a side reaction [7]. At the end, after the several washing processes, unfixed reactive and hydrolysed dyes remain in the dyeing wastewater [8].

Anthraquinone dyes can yield well-developed reversible reduction peaks, corresponding to the reaction of the quinone group in aqueous medium [9], as indicated in Figure 2.

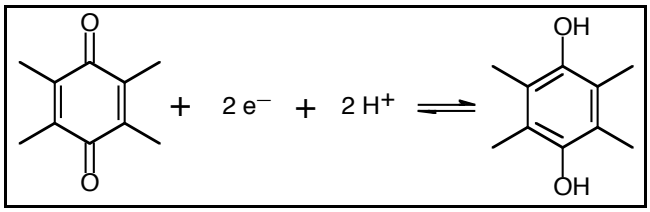

Figure 2 – Reversible electron transfer for a quinone group of an anthraquinone system

This system develops a reversible pair of peaks and, since this part of the dye molecule is the chromophore group, a change in the cyclic voltammogram is expected during electrochemical treatment, at the same time colour removal occurs.

2. EXPERIMENTAL

2.1. Dyebath preparation

Simulated dyebaths were prepared according a composition commonly used for cotton dyeing. Reactive Blue 19 was included in concentration 3% (o.w.f.). Among the several auxiliary products, NaCl and NaOH are fundamental for the establishment of dyeing conditions. By this reason, no support electrolyte was added for voltammetric measurements.

2.2. Experimental procedure

i) Electrochemical oxidation

Electrolysis apparatus consisted of a 400 mL closed cell and two Ti/RuO_2 electrodes,1.5 cm apart from each other and dipped in the wastewater. Magnetic stirring was used. The total effective electrode surface area was 62 cm^2. A power unit Farnell 30-10 controlled the power input. Potential values of 4, 6 and 8 V were applied in controlled potential experiments. Electrolysis with different duration was considered. Conductivity, pH, redox potential, COD and colour measurements were made using standard methods. Experiments were carried out at room temperature.

ii) Cyclic voltammetry

Voltammetric measurements were carried out using a potentiostat HI-TEK DT2101 and a galvanostat HI-TEK PPR1, controlled by an electrochemical software Picolog. The cell used for cyclic voltammetric experiments was an Amel three electrode type. The working electrode was a Metrohm glassy carbon disc, of 0.3 mm diameter, polished between experiments. An Ingold Pt auxiliary electrode and an Ingold SCE were used as the counter and reference electrodes, respectively. Experiments were carried out at room temperature.

3. RESULTS AND DISCUSSION

Different dye concentrations were considered, by dilution of initial dyebath. Selected values were 5, 10, 15 and 20% of original dyebath. Dyebath characteristics before and after electrochemical treatment, until total colour removal, are presented in Table 3.

Table 3 – Dyebath characteristics before and after electrochemical treatment, until total colour removal

Sol. (%)	App.Pot. (V)	pH		Conductivity (mS/cm)		COD (mgO_2/L)		Redox Potential (mV)	
		In.	Fin.	In.	Fin.	In.	Fin.	In.	Fin.
5	4	11.54	11.91	82.70	84.90	1581	365.20	156	458
	6	11.54	11.90	82.70	85.30	1581	238.96	156	488
	8	11.54	11.86	82.70	90.04	1581	222.73	156	506
10	4	11.91	11.55	77	80.50	1604	407	160	467
	6	11.91	11.57	77	81.60	1604	354.04	160	493
	8	11.91	11.64	77	82.30	1604	234.23	160	510
15	4	11.91	11.76	85.20	86.40	1934	325	190	475
	6	11.91	11.74	85.20	87.90	1934	439	190	504
	8	11.91	11.65	85.20	92.30	1934	356	190	509
20	4	11.51	11.71	83.40	85.30	2280	621	197	538
	6	11.51	11.75	83.40	87.70	2280	467	197	555
	8	11.51	11.81	83.40	91	2280	307	197	567

Electrochemical treatment results show mainly, significant decrease on COD values, as indicated in Figures 3 and 4, for the two limit values of dye concentration and the several applied potentials.

There is a considerable decrease on COD values after electrochemical treatment. In the first case, 5% of initial dyebath, best efficiency seams to correspond to 6V potential (there is no significant difference with results at 8V potential). In the case of 20% of initial dyebath, best COD removal is reached at 8V. In this circumstances, a more important variation can be detected between COD removal at 6 V and 8 V.

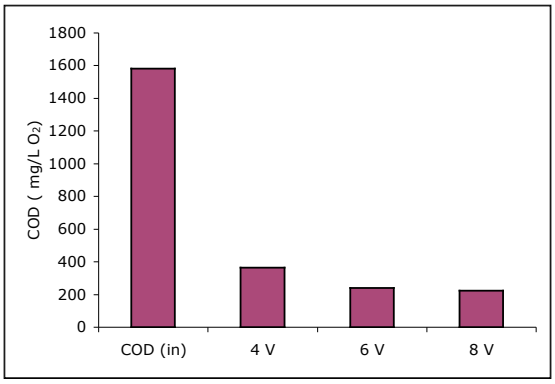

Figure 3 – COD values before and after electrochemical treatment (5% of initial dyebath)

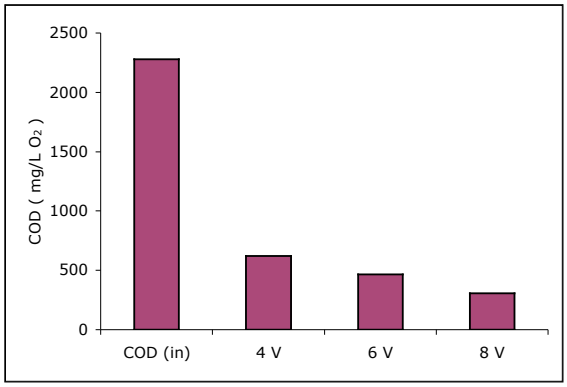

Figure 4 – COD values before and after electrochemical treatment treatment (20% of initial dyebath)

Progressive colour removal and dye degradation can be achieved, as shown in Figures 5 and 6, for the two limit values of dye concentration. Depending on electrolysis time and applied potential, total colour removal can be attained.

In the first solution (5% of initial dyebath), complete colour removal is reached, at 8 V, after 15 minutes of electrochemical treatment. With 6 V potential, identical situation is achieved after 20 minutes. A longer time is needed for a lower applied potential (30 minutes, for 4 V). 6 V seams to be an adequate and sufficient potential

for complete colour removal in these experimental conditions. In the case of the concentrated solution (20% of initial dyebath), about 65 minutes are required for colour removal at 4 V. At 6 and 8 V, 35 and 25 minutes are necessary, respectively.

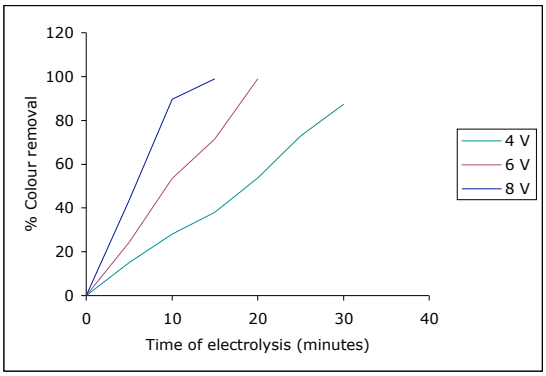

Figure 5 – Colour removal after electrochemical treatment (5% of initial dyebath)

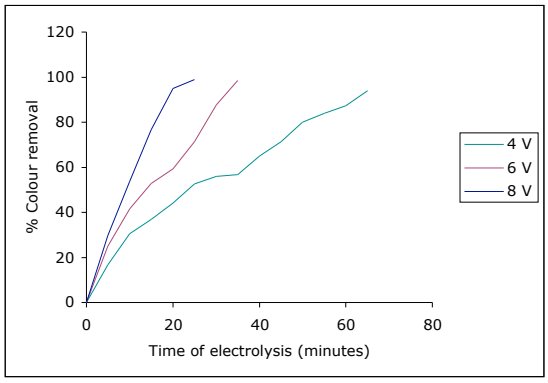

Figure 6 – Colour removal after electrochemical treatment (20% of initial dyebath)

In Figures 7 and 8 cyclic voltammograms of the less concentrated dye solution (5% of initial dyebath), before and after electrochemical treatment (6 V, until complete colour removal), are presented.

Before electrochemical treatment, the cyclic voltammogram presents a cathodic peak at about –360 mV, due to anthraquinone group reduction to hydroquinone derivative, after two electron transfer. This behaviour has been reported in several other studies, although with different working electrode material [10,11]. An anodic peak is also remarked, due to the reverse reaction. After treatment, reduction peak is no more perceptible and the solution is colourless. This result can illustrate the dye degradation (at least, the anthraquinone moiety degradation) by the electrolytic process.

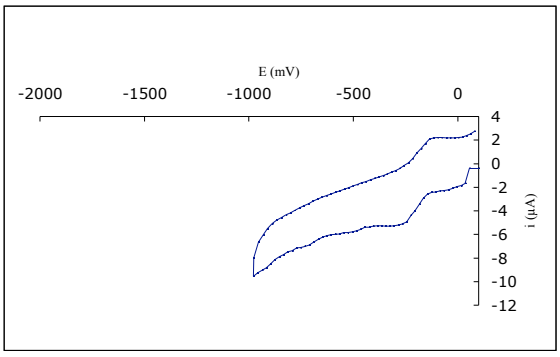

Figure 7 – Cyclic voltammogram (first scan) of dye solution before electrochemical treatment (5% of initial dyebath); glassy carbon; SCE; scan rate 20 mVs^{-1}

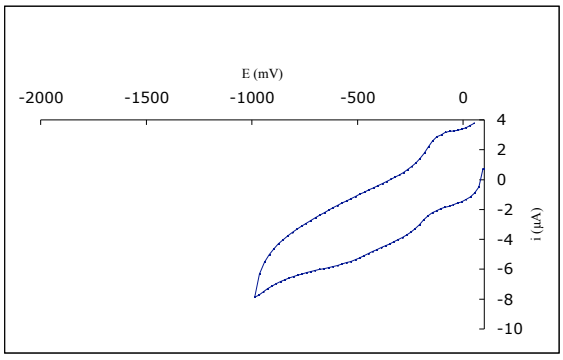

Figure 8 – Cyclic voltammogram (first scan) of dye solution after electrochemical treatment, until total colour removal (5% of initial dyebath); glassy carbon; SCE; scan rate 20 mVs^{-1}

4. CONCLUSION

The electrochemical techniques are an important alternative for treatment of textile wastewater. In the case of dyebaths, the indirect electrochemical oxidation seams to be an efficient procedure to complete COD and colour removal.

Adequate experimental conditions (applied potential and time of electrolysis) must be investigated and optimized for each type of effluent (high or low concentration of dyestuff). In the case of Reactive Blue 19, results showed that correct conditions are applied potential of 6 V and electrolysis time of 20 and 35 minutes, for the lowest and higher dye concentration, respectively. Under these conditions, significant reduce on COD values is achieved as well complete colour removal.

Cyclic voltammetry appears to be an attractive technique to follow the degradation of anthraquinone-based reactive dyes. In this case, the electrochemical degradation of the dye can be investigated and confirmed, step-by-step, by the disappearance of the reduction and oxidation peaks in the voltammograms.

Despite the complete colour removal and decrease on COD values of prepared dyebaths, an optimal solution acceptable to textile wastewater treatment must considerer electrochemical procedure in combination with other techniques. This must be necessary before eventual discharge or recycling of treated effluent.

5. REFERENCES

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